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CITATION:

Yamada, Takeshi ...[et al]. Automated Coulopotentiographic Analyzer for Trace Metal Ions. Bulletin of the Institute for Chemical Research, Kyoto University 1978, 56(5): 225-241

ISSUE DATE:

1978-12-20

URL:

http://hdl.handle.net/2433/76796

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 56, No. 5, 1978

Automated Coulopotentiographic Analyzer for Trace Metal Ions

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Received March 16, 1978

A new automatically controlled coulopotentiograph system for the trace analysis of metal ions has been developed.

The system is composed of four column electrodes, *i.e.* for the purification of base electrolyte, the elimination of disturbing components, the pre-concentration of trace object element and the detection. The electrode potential of each cell is controlled automatically by a timer program controller. Trace metal ions down to 10^{-8} mol/l were determined automatically.

A computer controlled analyzer system has been also developed where an automatic coulopotentiograph is placed under flexible control of a mini-computer.

INTRODUCTION

Constant potential coulometry has the great advantage of an absolute method of analysis based on Faraday's law. Conventional coulometry, however, goes only part of the way toward an ultra-trace analysis of metal ions because of the following defects; First, it takes a relatively long electrolysis time and is not sensitive enough; Second, the simultaneous determination of multi-components system is difficult; And third, the pre-concentration and the stripping steps from very dilute sample solutions are not convenient.

The authors have overcome these disadvantages of the conventional coulometry in the course of studies on rapid electrolysis with a column electrode.[1-5] In particular, as reported previously, the stripping coulopotentiography[6,7] with double-cells enables the trace analysis of lead ions of a concentration as low as 10^{-8} mol/l, by eliminating the effect of the charging current caused by potential scanning. Strictly speaking, however, even this method still has the following difficulties which are also unavoidable in most trace electroanalyses; (1) The determination limit is restricted by the amounts of the impurities contained in the supporting electrolyte. (2) Complete dissolution of the deposited trace metal is prevented by co-deposition of pre-discharging metals. (3) Difficulties in setting up an exact pre-concentrating time.

In the present paper, the authors have developed a fully automated coulopotentiographic analyzer system for the trace analysis of metal ions. Four flow cells were used to get over those difficulties mentioned above, *i.e.*, use of the purification cell, the gate cell, the pre-concentration cell, and the detector cell.

For the controlling system of the operations of these four column electrodes, two

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kinds of the system have been developed in the course of the studies. These are, an automated system with timer controller and a computer controlled one. In the latter, the authors successfully utilized a mini-computer not only as an operating controller but also as a data processor.

This newly developed automatic coulopotentiographic analyzer system was found to be useful for the automatic trace analysis of metal ions at ppb level.

EXPERIMENTALS

Reagents

All the chemicals used were of analytical reagent grade. Deionized water was used after distilled from an all quartz ware. Supporting electrolyte carrier solution contained 2 *M*-NaCl, 0.1 *M*-KI, and 0.1 *M*-CH_3COOH gave very small residual current. Sample solutions were acidified with acetic acid to keep very dilute metal ions stable. 1 *M*-KCl solution was used for the counter chamber electrolyte. A saturated silver-silver chloride reference electrode (SSE) was used.

Instruments

Figure 1 shows the schematic diagram of the system. An auotmatic coulopotentiograph was manufactured by Shibata Chemical Instruments Co. Ltd.

Flow cell system: Four flow cells in the figure were the same column electrodes with glassy carbon grains as reported in the previous paper.[7]

Cell 1 is a purification cell to remove the metal impurities in the supporting electrolyte solution by constant potential electrolysis.

Cell 2 is called a filter cell or a gate cell owing to its functions. During the concentrating period, it serves as a filter to eliminate only interfering ions of more noble metals. Then, in the stripping period, it works as a gate cell to cut off even the objective ions.

Cell 3 is used for pre-concentrating of trace target metal ions and selective stripping of deposited objective metal.

Cell 4 is a detector to determine the eluted target ions by constant potential flow coulometry.

Potentiostats: Potentiostats 1 and 4 are of the conventional type; *i.e.* cell 1 is for constant potential electrolysis and cell 4 is for the use of coulometric detection. Potentiostat 4 is equipped with a recorder output terminal to measure the electrolysis current flowing through a sensitivity resistor of 10 or 100 ohm, and a base current compensator potentiometer.

Potentiostat 2 is equipped with dual potentiometer dials. One of two set up potentials is turned on by an external signal from a control unit.

Potentiostat 3 is equipped with a potential scanning unit, which is triggered by an external signal from a control unit and stops automatically at the pre-set potential. The rate of potential scanning is selectable from 0.1 mV/min to 500 mV/min, and the range of potential scanning is 1.2 V max. This potentiostat is also equipped with a recorder output terminal to measure the scanning voltage.

Figure 2 shows the circuit of potentiostat 3. In the figure, block 1 shows a constant

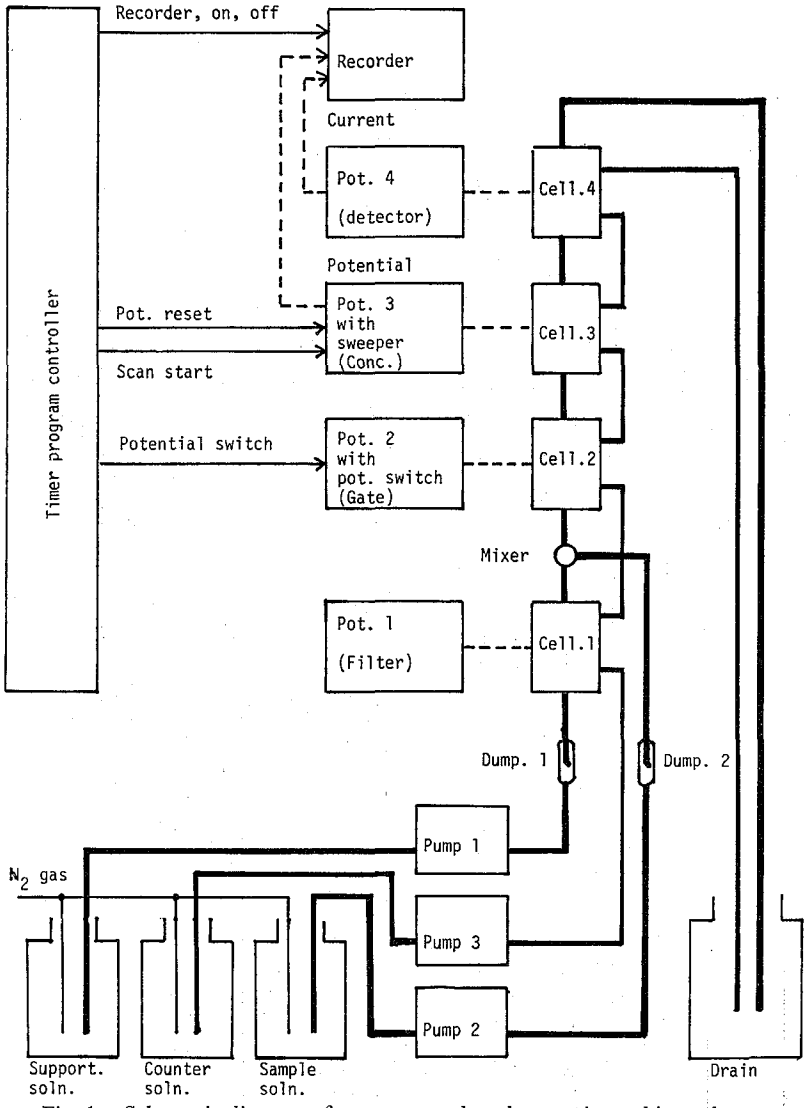


Fig. 1. Schematic diagram of an automated coulopotentiographic analyzer.

potential electrolysis circuit, and block 2 shows a potential scanning circuit. The latter consists of an integrator circuit using the operational amplifires and has such functions as potential scanning, holding and resetting. Block 3 shows a control circuit which decodes the signals sent from the timer controller and sends such orders as potential scanning, holding and resetting to block 2. Block 4 shows a potential scanning range detector circuit, which sends scan end pulses to block 3 and to the timer controller to make the potential scan and hold.

Timer program control unit: A circuit of the timer program control unit is shown in Fig. 3. The period of the concentration, delay, stripping and cleaning times are set by four timers from *T*-1 to *T*-4, respectively. Each timer sends a control signal to each potentiostat or a recorder: *i.e.* order potentiostat 3 potential scan and reset, and order potentiostat 2 potential switch, and order the recorder start or stop. These controlling functions

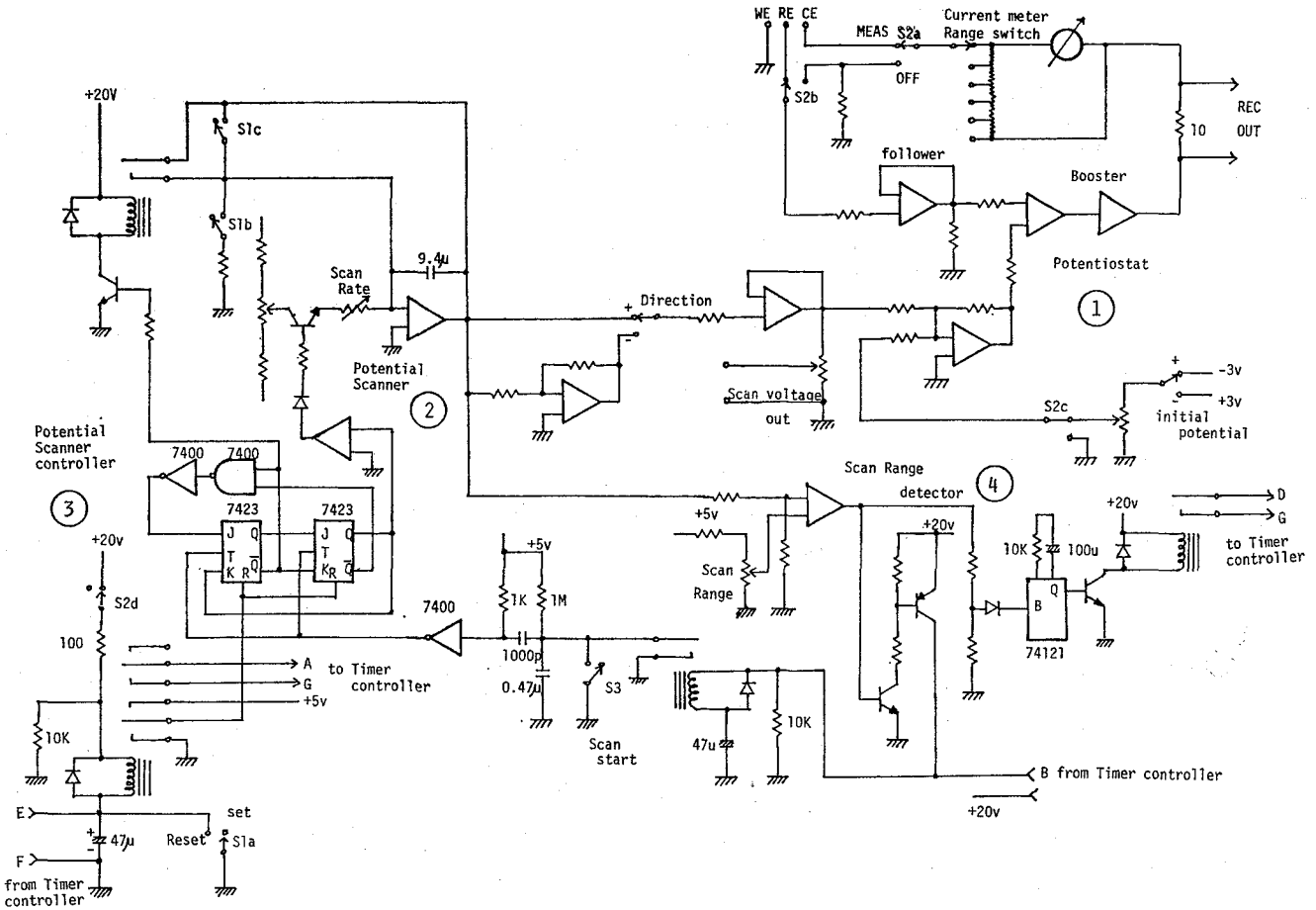


Fig. 2. Schematic of a potentiostat 3 circuit.
1: Potentiostat, 2: Potential scanner, 3: Potential scanner controller, 4: Scan range detector.

are carried out as follows; Signal (A, G) from potentiostat 3 turns relay 1 on, then timer 1 starts. When the timer 1 reaches to the pre-set time, the contact of timer 1 closes and relays 2 and 3 work. As a result, the potential switching signal (1, 2) and the recorder start signal (1, 3) are sent to potentiostat 2 and recorder. When the timer 2 reaches to the pre-set time, the contact of timer 2 closes, relay 2 opens, relay 4 closes momentarily, and relay 5 closes. Thus the potential scanning signal (B, G) is sent to potentiostat 3 to start the potential scan. After completing the potential scan, potentiostat 3 sends the scan end signal (D, G) to the timer control unit, at which time relay 6 closes, and timer 3 begins to work. When timer 3 reaches to the pre-set time, the contact of timer 3 closes, relays 3 and 5 are opened and relay 7 is closed to reset the potential of potentiostat 2 and stop the recorder. In addition, relay 7 causes timer 4 to start. When timer 4 reaches to pre-set time, the contact of timer 3 is open, and

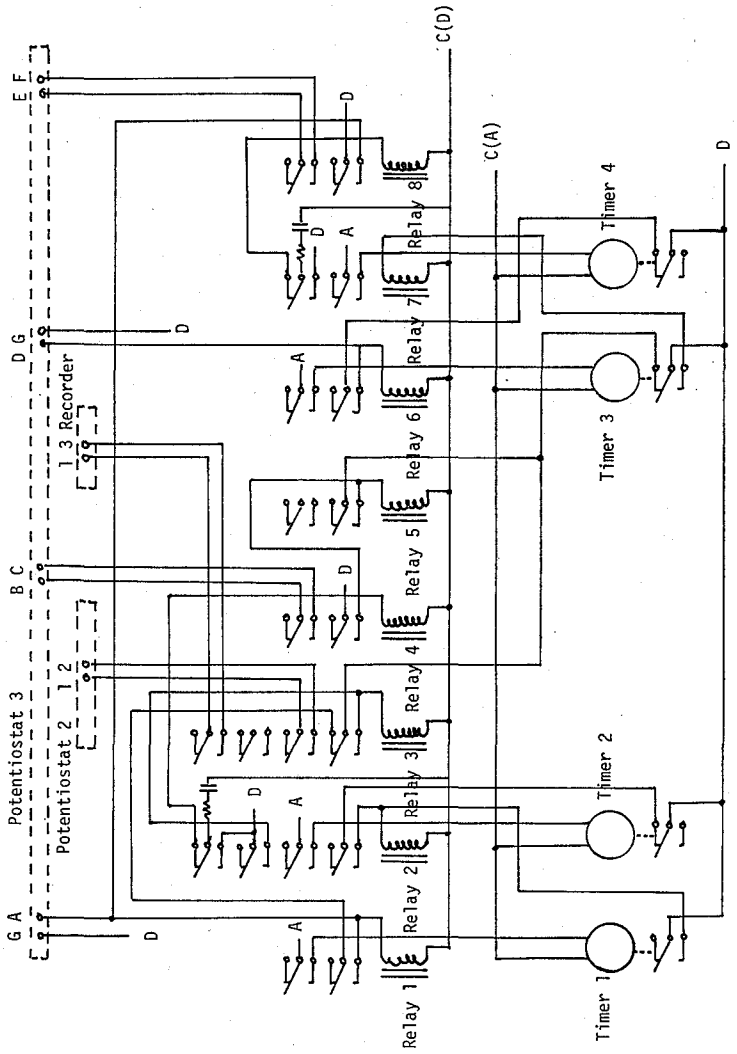


Fig. 3. Timer controller unit.
D: DC source, C(D): DC common, A: AC source, C(AC): AC common.

relay 8 is closed momentarily. Then the potential of potentiostat 3 is reset (E, F) and relay 1 starts. As a result, the next cycle begins.

In this manner, the device works automatically such actions as purification and separation, pre-concentration and selective stripping, conditioning and cleaning of the column electrodes, and recording the electrolysis current and the scanning voltage. Timings of these actions are selectable using each timer from T-1 to T-4.

Procedures: The operation procedures for the determination of the trace amounts of metal ions are explained according to Fig. 1 as follows;

Carrier, sample and counter chamber electrolyte solutions, after deoxygenated by bubbling nitrogen gas, are fed through each column electrode in turn at a constant flow rate of 1 ml/min by constant volume pumps 1, 2, and 3, respectively. The sample solution, after being mixed with the carrier solution which has been purified by pre-electrolysis at cell 1, passes through cell 2 to remove the greater part of the more noble metal impurities. At the third cell, the objective metal ions are pre-concentrated with potentiostat 3 for a definite period of time. After the concentration step, the potential of cell 3 begins to sweep to strip out the deposited objective metal. The eluted target ions are determined at cell 4 by constant potential coulometry. The stripping coulopotentiogram is obtained by recording the electrolysis current of cell 4 against the stripping potential of cell 3.

The timing chart of the operation procedure is shown in Fig. 4. The potentials of cell 1 and 4 are kept constant throughout the operation. The time interval from t_0 to t_1 is a concentration time and is selectable from 1 sec to 60 hrs with a multi-range timer. At the time t_1, the potential of cell 2 is switched to the more negative one to remove not only pre-discharging metals but also the object metal, and the recorder starts. There is a time delay from t_1 to t_2 to avoid the influence of the potential change upon the background current of cell 4. At the time t_2, the potential of cell 3 begins to scan in the positive direction to dissolve the deposited objective metal. The potential scanning of cell 3 stops at the time t_3 and is held until t_4 to allow the complete stripping of the objective metal without elution of the pre-discharging metals. Though the stripping period should be finished at t_3, the standing time from t_3 to t_4 is prepared due to the time delay caused by the dead volume between cell 3 and cell 4. The term from t_4 to t_5 is the cleaning time to strip out the objective metal which may have deposited during the time interval from t_1 to t_4. At the last time t_5, the potential of cell 3 is reset to the next pre-concentration, and the next analysis cycle is ready to start.

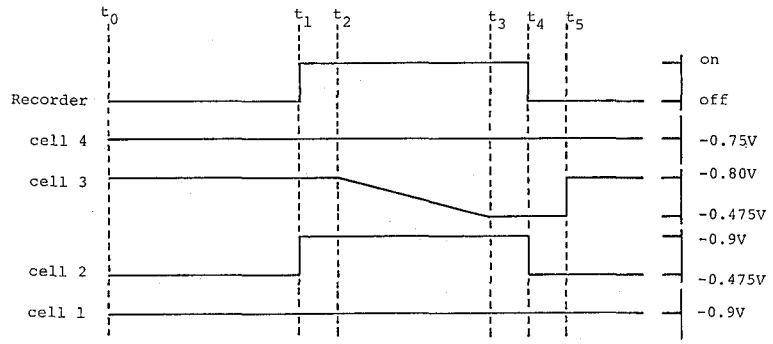


Fig. 4. Timing chart for trace analysis of Pb^{2+}.

Operating Conditions for the Analysis of Trace Lead Ions

In case of the trace analysis of lead ions under the co-presence of copper ions, the potential of each electrode was set as follows; The potential of cell 1 was chosen sufficiently negative as −0.90 V *vs.* SSE. The potential of cell 2, during the pre-concentration term, was set at −0.475 V *vs.* SSE to make copper ions deposit, but lead ions pass through the cell. During the stripping term, however, the potential of cell 2 was switched to −0.9 V *vs.* SSE to cut off lead ions as well as copper ions. The delay time from t_1 to t_2 was 1 min. The pre-concentrating potential of cell 3 was chosen to be −0.80 V *vs.* SSE to allow the complete deposition of lead. After the concentration step, the potential was scanned from −0.8 to −0.475 V *vs.* SSE to strip away the deposited lead perfectly. The standing time from t_3 to t_4 and the cleaning time from t_4 to t_5 were set 2.5 and 5 minutes, respectively. The potential of cell 4 was kept at −0.75 V *vs.* SSE throughout the operation to detect the eluted lead ions by constant potential coulometry.

Determination of Trace Lead Ions

The availability of purification cell 1 was tested by electrolyzing the supporting electrolyte solution for three hours at a flow rate of 1 ml/min. No lead peak was found in the elution curve. Copper ions, however, were removed incompletely even at such negative potential. The amounts of lead impurities were to be at ppb level.

The sample solutions containing lead ions from 2×10^{-8} mol/l to 2×10^{-7} mol/l were analyzed by this method with a pre-concentrating time from 15 min to 120 min. Determinations were carried out by weighing the peak area of the chart which was initially substracted from the base current. The results obtained are summarized in Table I.

Electrolysis efficiencies varied slightly not only with the concentration of the sample

Table I. Determination of trace lead ions.
Carrier soln.: 1 *M* NaCl+0.1 *M* KI+0.1 *M* CH_3COOH, sample flow rate: 1 ml/min, concentration potential: −0.8 V *vs.* SSE.

Concentration ($\times10^8$ mol/l)	Concentration time (min.)			
	15	30	60	120
20	101.7	96.4	101.0	99.7
	101.5	96.3	96.5	100.6
	101.5	95.9	95.2	97.9
10	107.2	104.4	108.7	95.3
	105.0	105.4	100.9	94.3
	112.3	101.9	102.3	
5	119.5	110.9	97.9	
	117.5	109.4	98.4	
	121.6	107.0	94.6	
2		149.1	122.1	133.2
		141.9	121.2	117.6
		118.8	121.4	109.8

but also with the pre-concentration time and was inclined to increase with decreasing concentration of lead ions and also with decreasing concentration time. These tendencies seemed to be due to the fact that the residual current of cell 4 was still influenced by the potential change of cell 3.

COMPUTER CONTROLLED ANALYZER SYSTEM

Hardware

A computer controlled coulopotentiographic analyzer system has been developed to impose the more flexibility by combining the automatic coulopotentiography with a mini-computer through an interface instead of the timer program unit.

A mini-computer used was a HITAC-10[8] (with 8 *KW* core memory, an extended arithmetic unit, a data typewriter and a photo tape reader) from Hitachi. The interface circuits were newly developed for this system using *TTL*'s, operational amplifiers and a Teledyne-Philibric voltage-to-frequency (*V/F*) and a digital-to-analog (*D/A*) converters.

The schematic block diagram of this system is shown in Fig. 5. The central processing unit (*CPU*) takes care of every data transfer to and from the typewriter and the interface. The interface decodes instructions from CPU to each control unit. The recorder control unit converts digital data to analog data and controls recorder on/off to draw the coulopotentiograms. The cell 4 control unit converts electrolysis current at potentiostat 4 to digital data. The cell 3 control unit gives potential scanning and reset signals to potentiostat 3. The cell 2 control unit switches the potential of potentiostat 2.

Detailed illustrations of the interface logics are given in Figs. 6, 7, 8, and 9. Figure 6 shows the interface board 1 which includes the device selecting circuit and the command decording one. The latter decodes instructions from *CPU* to the interface. The former works the interface when *CPU* call this interface. The interface board 2 of Fig. 7, consists of multi-level interrupt priority encoder and the interrupt reset decoder. As a vector interrupt handling method adopted, the burden of software decreases considerably. The next drawing shows the analog input board. A *V/F* converter having a capacity of 1 MHz/10 V and a 20 bit counter were used as an analog-to-digital (*A/D*) converter. This *A/D* converter has a wide current range from 50 pA to 50 mA when the sensitivity resister of potentiostat 4 is 100 ohm, and the sampling interval is 2 sec. The use of a *V/F* converter as an *A/D* converter makes a great advantage of a good signal-to-noise ratio owing to its intergration effect, as well as a wide dynamic range of 10^6. Figure 9 shows the output board, in which the analog ouptut, the instrument control and timer circuits are included. A 10 bit *D/A* converter is used to output analog data. Each instrument of the analyzer is controlled by means of relays which separate the instrument electrically from the interface. The timer circuit is used to determine sampling interval and sequential control of the analyzer. The available intervals are 0.1 or 1 sec.

Software

Whenever, the computer does calculation, recording, typewriter input/output and

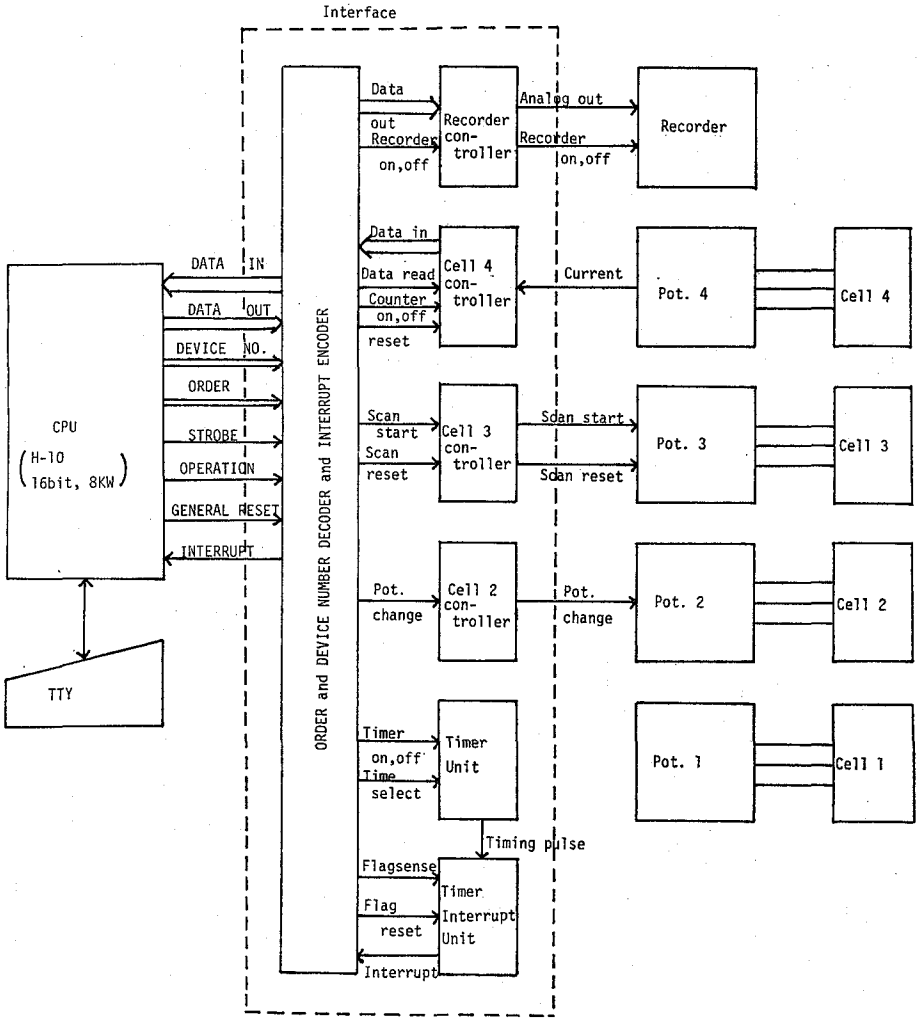


Fig. 5. Block diagram of a computer-controlled coulopotentiographic analyzer system.

so forth, the computer controlled coulopotentiographic analyzer must control each element without any prevention. Therefore, real-time operating system is necessary. Software support of a real-time operating system which works in multi-task environment was not offered to such a small computer system, however. The authors developed an operating system "*micro OS*" which is small in size (1 *KW*) but powerful enough and appropriate to handle multi-task scheduling in this application. The *micro OS* replies to interruptions from the input and output units in a very short break of the currently working program and several works are available at the same time.

The hierarchical structure of software system is illustrated in Fig. 10. The highest priority program assigned to level 0 is carried out in the interrupt-disable mode. The interrupt analysis program, the task control program and the command analysis program make up the *micro OS*. The floating-point arithmetic package and the common utility package are composed of many subroutines, which are widely used in each program. The data analysis program does detection and calculation of peak area on

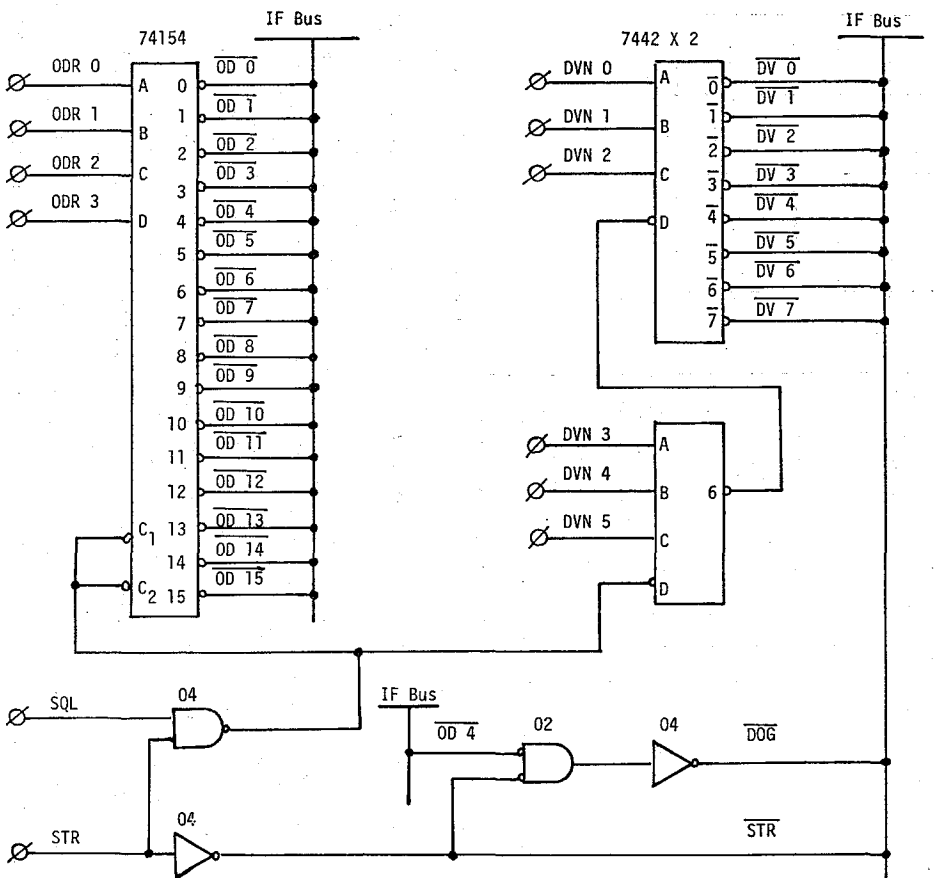
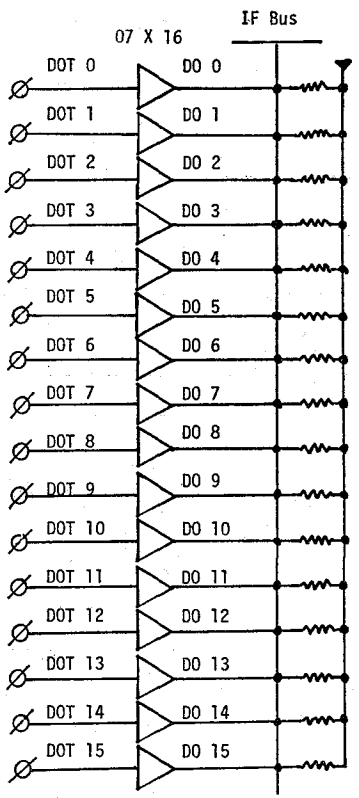


Fig. 6. Interface board 1.
ϕ: CPU connector



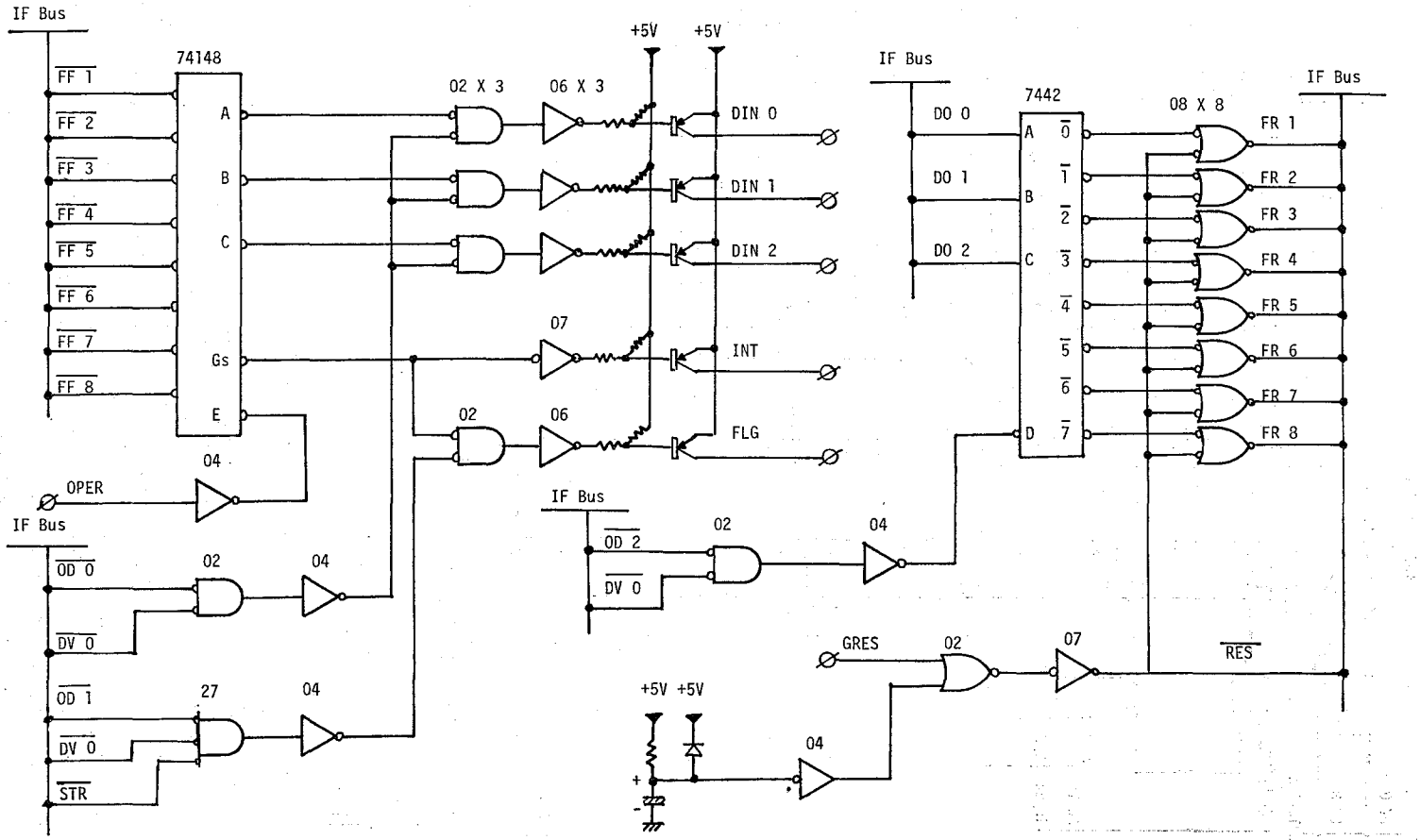


Fig. 7. Interface board 2.

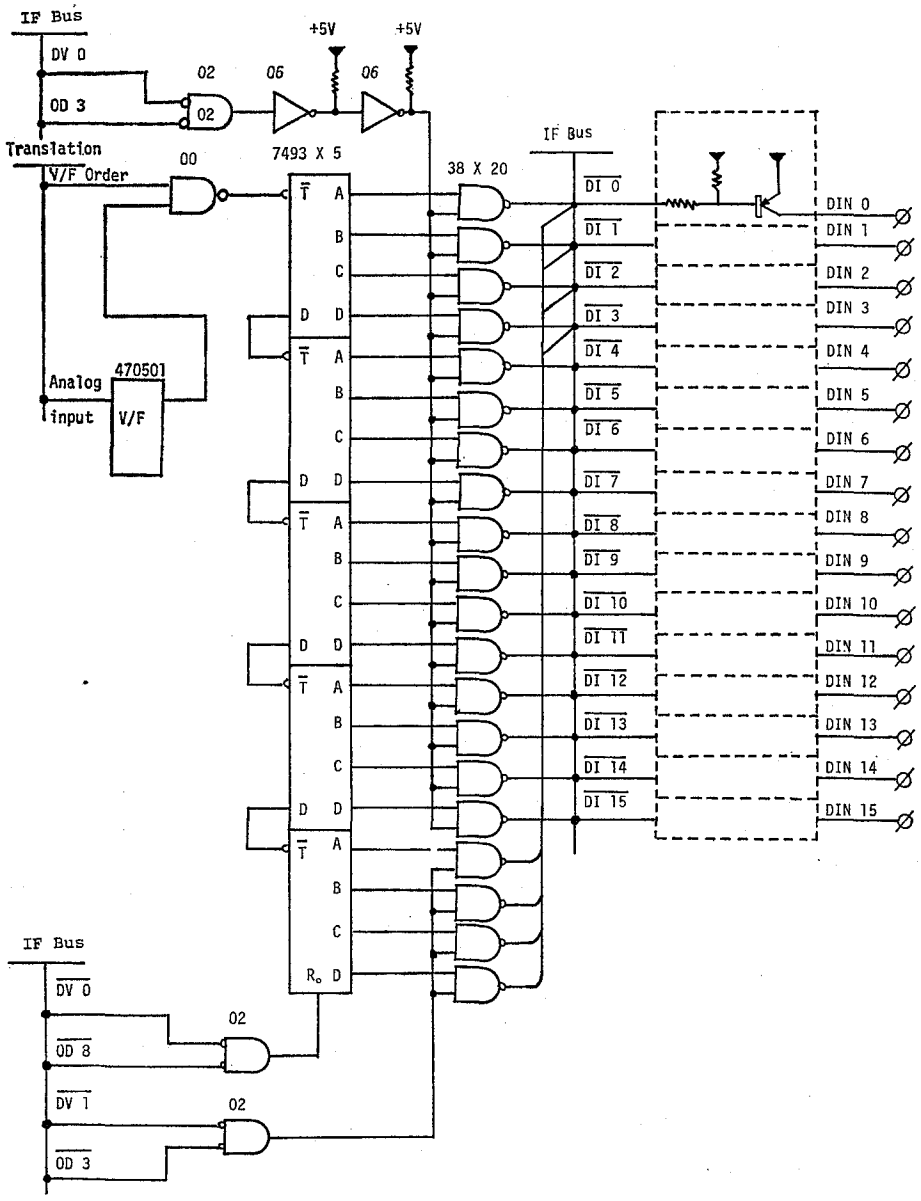


Fig. 8. Analog input board.

the coulopotentiogram and transfers the curve to the recorder. The loop program is an idle program which works only when the other programs are all reset.

Two working modes of coulopotentiograph are available as shown in Fig. 11. On *mode* 0 which corresponds to that of the automated coulopotentiographic analyzer with the timer program unit, concentration time is (t_0-t_1) and the ratio of effective concentration time to total analysis time is given by $(t_0-t_1)/(t_0-t_5)$ and is not so efficient. This means that the objective ions are concentrated for the time period between t_1 and t_4 and then are stripped out for the term from t_4 to t_5.

On *mode* 1, on the other hand, the ratio of the effective concentration time to the

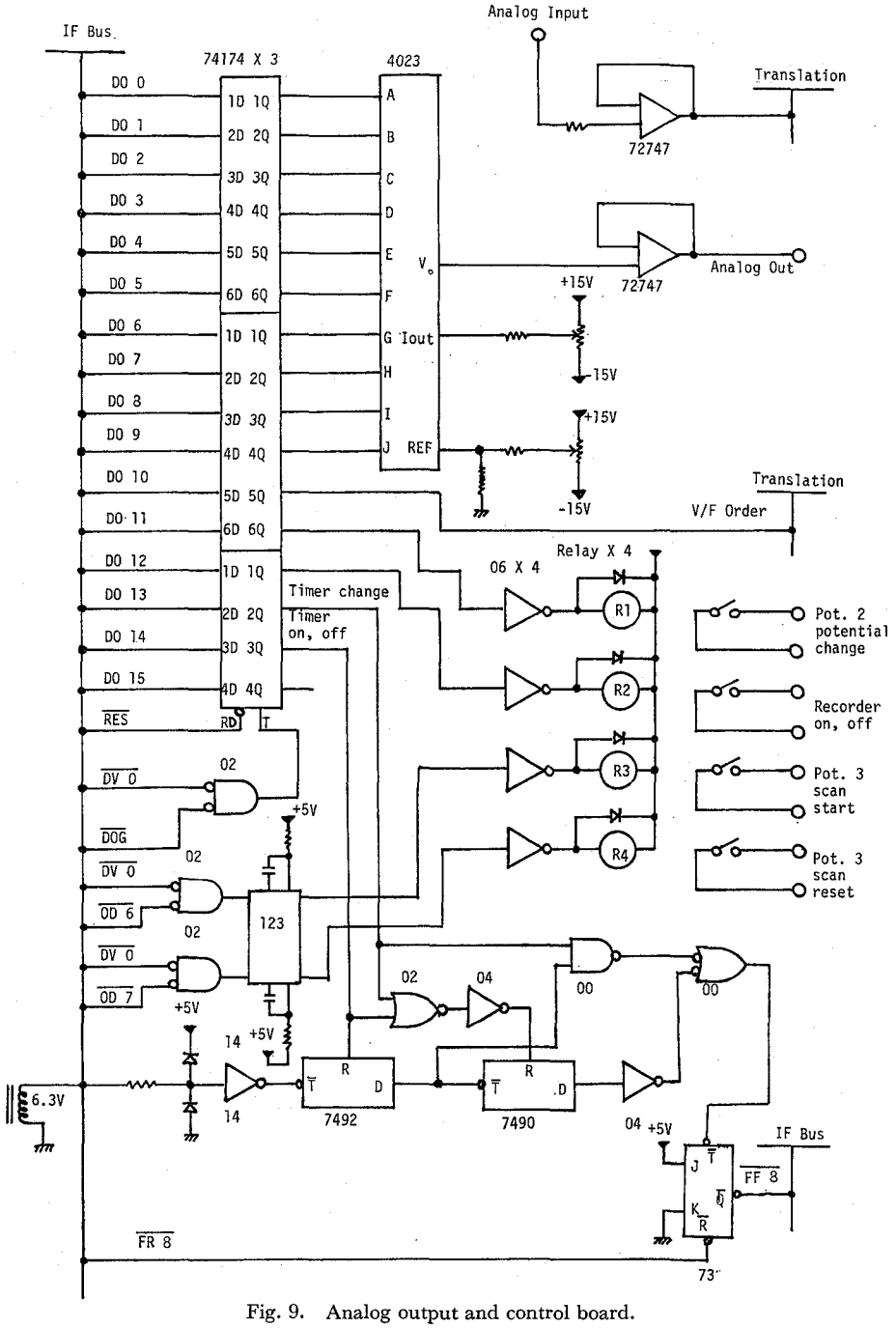


Fig. 9. Analog output and control board.

total analysis time is unity. This is because that the concentrated metals during the term between t_1 and t_5 is re-deposited again after t_5. It is said that *mode* 0 is effective for a very short concentration time and *mode* 1 is effective for the longer concentration time.

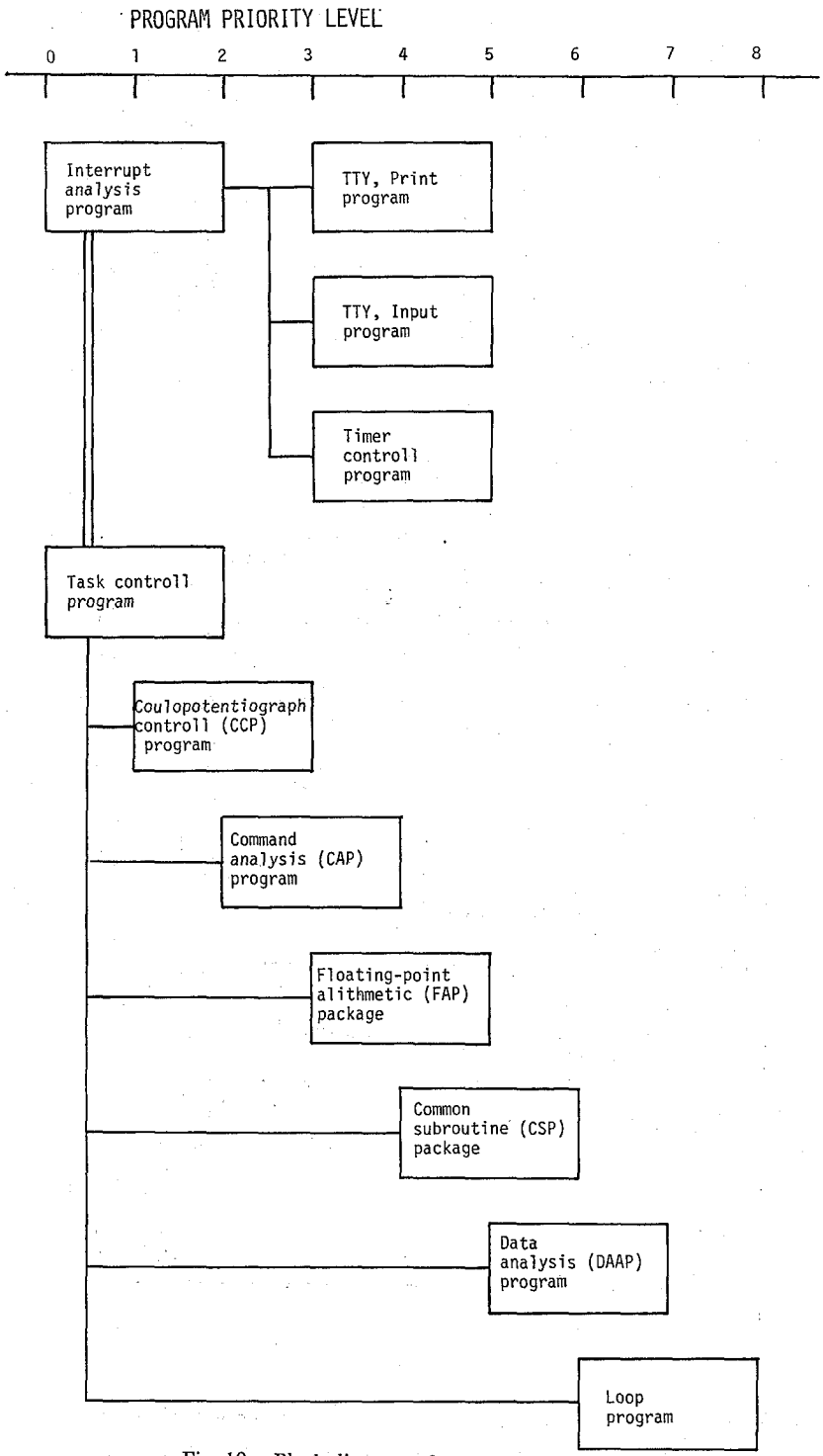


Fig. 10. Block diagram of a software system.

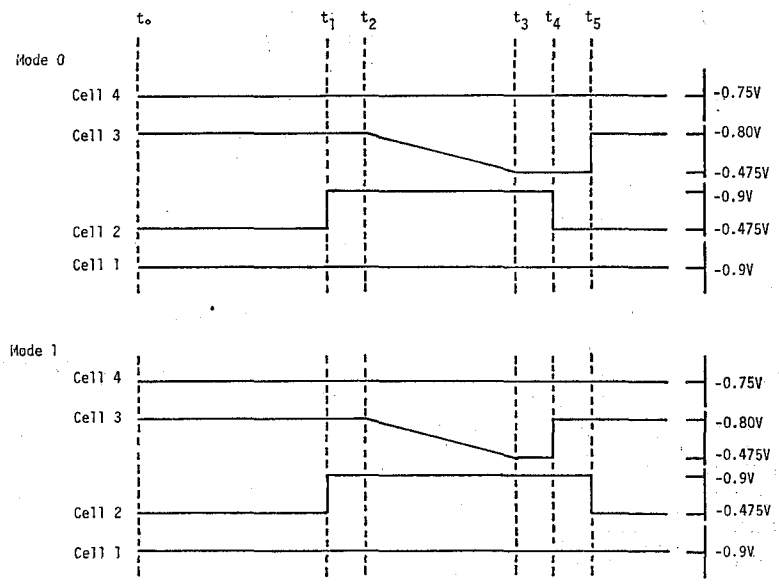


Fig. 11. Timing chart of a computer-controlled analyzer.

Analysis of Lead Ions

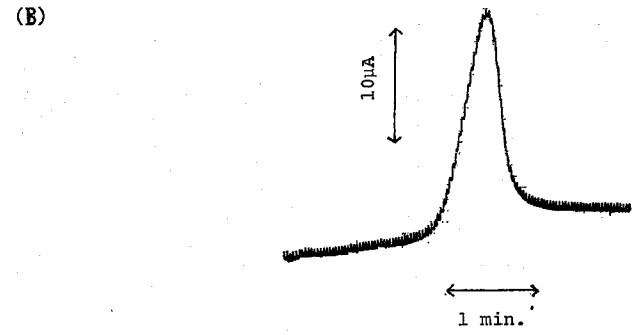
A standard sample of 1.5×10^{-7} mol/l Pb^{2+} was analyzed by this method. A typical example of stripping curves obtained in this method (curve A) and direct recording (curve B) are shown in Fig. 12. The coulopotentiogram in this method looks like a histgram with an interval of 2 sec. The noises that appeared in curve B almost disappear in curve A. Pulse 1 in the figure shows the data number and pulse 2 shows the scale. The stripping curve is initially subtracted from the base current and is normalized to avoid over scale. Analytical conditions are also printed out. For *mode* 0, timer 1 shows a concentration time of (t_0–t_1), timer 2 shows a delay time of (t_1–t_2), timer 3 shows a stripping time of (t_2–t_4), timer 4 shows a cleaning time of (t_4–t_5), timer 5 shows the potential hold time after scanning (t_3–t_4) and timer 6 shows the potential scanning time (t_2–t_3), respectively. For *mode* 1, timer 1 corresponds to (t_0–t_5). Timer 6 is calculated from the potential scanning rate and scanning range. Timer 3 is the sum of timer 5 and 6. Timer 7 is used as a safety device on *mode* 1.

Results of the determination are also printed out. Those show that the sample number is 0, concentration is 0.305×10^{-6} N, the concentration time is 10 min, and the peak potential is -535 mV *vs.* SSE.

CONCLUSION

As mentioned above, these analyzer systems have the great advantage for the automatic analysis of trace metal ions at ppb level. Further more, these systems will be easily applicable for the automatic monitoring of toxic metals in the hydrosphere such as sea water.

A system based on a timer program control unit is not only very simple and eco-




```
FLOW-RATE (ML/MIN.) =  0.50000E+01  SCAN-RATE (MV/MIN.) =  0.20000E+01
SCAN-RANGE (MV) =  0.31500E+03  MODE =+000
INITIAL POTENTIAL (MV) =-0.85000E+03
STOP POTENTIAL (MV) = -0.53500E+03
TIMER +001 =+010 MIN. +000 SEC.
TIMER +002 =+002 MIN. +000 SEC.
TIMER +003 =+004 MIN. +037 SEC.
TIMER +004 =+002 MIN. +000 SEC.
TIMER +005 =+002 MIN. +000 SEC.
TIMER +006 =+002 MIN. +037 SEC.
TIMER +007 =+002 MIN. +000 SEC.
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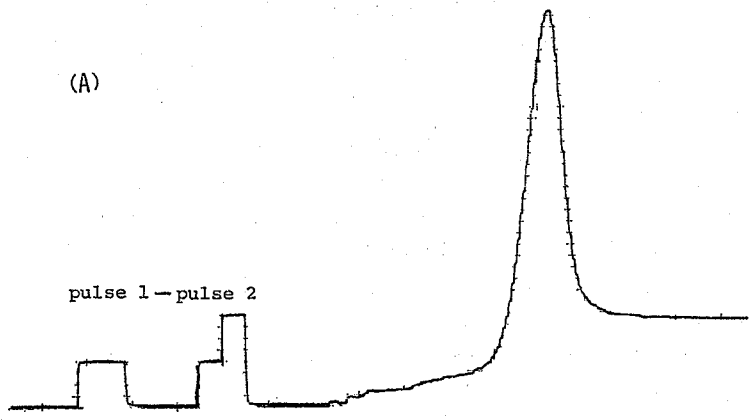


```
SAMPLE NO = +00000
CONCENTRATION ( N ) =  0.30504E-06
MODE =+00000
CONCENTRATION TIME =+00010 MIN. +00000 SEC.
PEAK POTENTIAL ( MV ) = -0.53500E+03
```

Fig. 12. Stripping coulopotentiogram of Pb^{2+}.
A: computer recording, B: direct recording of stripping current.

nomical in the instrumentation, but also sensitive enough to determine metal ions as low as 10^{-8} mol/l or less.

The use of the mini-computer brings a great variety of functions such as an automatic selection of pre-concentration time according to the sample and automatic real time data processing.

The further applications of the system are now under way and will be presented elsewhere.

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